

UTILIZATION OF WASTE

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USE OF CULLET OF DIFFERENT CHEMICAL COMPOSITIONS IN FOAM GLASS PRODUCTION

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The results of studying the possibility of using cullet of different chemical compositions accumulated at dumping grounds for foam glass production are described. It is established that sodium silicate introduced into cullet in the form of water glass partly destroys milled cullet and homogenizes the chemical composition of the batch and its most significant technological properties. Due to the chemical reaction between water glass and the surface of milled cullet particles, silicates are formed containing bound water, which is released at high temperatures (600–620°C) and facilitates frothing of foam glass. Water glass in a batch increases the quantity of the vitreous phase and decreases the propensity of glass for crystallization.

One of the topical environmental problems is utilization of the great quantity of household and industrial cullet accumulated at waste dumps. About 20% of waste glass can be collected, washed, sorted, and returned to glass factories for remelting. However, the major part of cullet is unsuitable for glass production. Another possible application area is production of foam glass.

According to the authors of [1, 2], high-quality foam glass with constant physicomechanical properties, volume weight below 180 kg/m³, water absorption below 5%, and an ordered structure can be produced only from glass of constant chemical composition, which cannot be ensured using waste of uncertain origin and variable composition.

Some authors [3–5] propose using cullet for foam glass production, but this cullet should have a stable composition. A method for recycling waste generated in kinescope production for foam glass has been patented (RF Patent No. 2176219). The initial material for granulated foam glass is broken sheet and container glass [3]. To improve the quality of foam glass (structure, density) and to lower the firing temperature, container glass cullet and nepheline sienite are added to a mixture containing volcanic glass and sodium hydroxide (RF Patent No. 2164898). Another patent proposes using bottle glass waste, sodium silicate, silicon oxide, and a foaming agent for foam-glass production (RF Patent No. 2167112). U.S. Patent No. 3963503 proposes a method

for producing foam glass from crushed container glass cullet. It is possible to use cullet with the following quantity of impurities (wt.%): 0.1–3.0 Fe, 0.1–2.0 Sn, 0.1–2.0 Al, 0.1–1.0 other metals, 0.1–1.0 paper, and 0.1–1.0 other organic impurities.

It is known (U.S. Patent No. 3870496) that cullet is treated by chemical agents introducing hydroxyl groups into its structure. When such cullet is heated to a temperature exceeding the softening point, OH groups are formed, which leads to foaming of modified cullet. The cullet is treated in water. Thus, foam glass with a rigid cellular structure is obtained.

It is indicated in [4, 5] that foam-glass granules of high porosity can be obtained from cullet by using water-soluble glass. An aqueous solution of water glass acts as a binder improving the formation of granules from container and building glass cullet (RF Patent No. 2162825).

Certain literature sources [6] report that increasing the amount of Na₂O to 18% facilitates the homogenization of some properties (for instance, softening temperature and surface tension) of glasses that have different chemical compositions.

According to the authors of [7], destruction of glass by alkali is a complex physicochemical process, as a consequence of which an intermediate layer is formed on the glass surface, whose composition and properties differ from the composition and properties of initial glass. Such alkali-treated glass samples melt at a temperature that is 50–100°C

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TABLE 1

Aqueous solution	Treatment conditions		Temperature of water for washing samples after treatment in alkali solution, °C	Weight loss of sample, %
	temperature, °C	duration, h		
Sodium water glass	18 ± 2	48	18 ± 2	1.7
	95 ± 5	4	18 ± 2	5.6
	18 ± 2	72	45 ± 5	6.4
	95 ± 5	4	45 ± 5	9.0
Caustic soda	18 ± 2	48	18 ± 2	2.7
	95 ± 5	4	18 ± 2	9.2

lower than the melting point of samples not treated by alkali solutions.

The authors of RF Patent No. 2167112 state their opinion that when silicate vitreous materials are treated with alkali, especially at elevated temperatures, the aqueous alkali solution reacts with silicon oxide, which leads to the formation of sodium silicate in the solution. Sodium silicate has binding properties and can bind silicate powders into strong composites.

We propose using sodium silicate in the form of water glass to homogenize the chemical composition of a mixture of different types of cullet. The purpose of the present study is to study the possibility of using cullet of different chemical compositions for foam glass production.

The study was performed on container and window glass cullet accumulated on dumping grounds. The cullet was crushed in a jaw crusher and milled in a ball mill to a specific surface area of 350 – 850 m²/kg. The specific surface area of milled cullet was measured using a PSKh-2 instrument. The modifier was water glass according to GOST 13078 (wt.%): 30.8 – 31.9 SiO₂, 11.0 – 12.1 Na₂O; silica modulus 2.62 – 2.89. The density measured with a densimeter at 20°C was equal to 1.41 g/cm³. The caustic soda complied with the requirements of GOST 4328.

The degree of reaction of cullet with the aqueous solution of water glass was determined by the amount of glass passing to a liquid state. The melting or softening temperatures of glass t_η corresponding to typical viscosities 10² Pa · sec (melting temperature at a viscosity 10² Pa · sec), 10⁴ Pa · sec (glass softening temperature; at a viscosity 10⁴ Pa · sec glass is deformed under the effect of its self weight), and 10⁸ Pa · sec (glass softening temperature; at a viscosity 10⁸ Pa · sec the glass is deformed under a mechanical effect) were calculated using the following formula [6]:

$$t_\eta = Ax + By + Cz + D,$$

where A, B, C, and D are constants for temperature calculation corresponding to certain glass viscosity values typical of Na₂O, (CaO + 3% MgO), Al₂O₃, and SiO₂, respectively; x, y, and z are the weight contents of Na₂O, (CaO + 3% MgO), and Al₂O₃, respectively.

The surface tension of melts was found based on the formula [8]:

$$\sigma = \frac{\sum \sigma_i a}{\sum a},$$

where σ_i are the melt surface tension factors of each oxide and a is the molar content of oxides, %.

The start temperature of glass melting was found using an MNO-2 high-temperature microscope. The rate of temperature rise was 10 K/min. Typical changes in the shape of samples were registered during the analysis. The structural changes occurring in firing of cullet were investigated using a DRON-2 diffractometer. The differential thermal analysis was performed in air using a Q-1500 Paulik – Paulik – Erdey derivatograph. The rate of temperature rise was 10 K/min.

The study considered the destruction of the surface of milled cullet particles of different chemical compositions. To do this, cullet milled to a specific surface area of 620 m²/kg was treated with an aqueous solution of water glass (1 part water glass : 1.5 parts distilled water). For reference purposes cullet was treated with 0.5 M caustic soda solution. It can be seen from the data in Table 1 that the degree of destruction of cullet grows with increasing temperature and duration of treatment.

Chemical analysis indicates (Table 2) that upon introducing Na₂O in the form of water glass solution to cullet typically found on waste dumping grounds, the quantity of the main component (SiO₂) virtually does not change, the content of Na₂O grows, and accordingly, the relative content of other oxides decreases.

Of all the physicomechanical properties characterizing a cullet-based batch for foam glass, viscosity and surface tension are the most significant for the hot foaming process. Variations in melting or softening temperatures of batches under characteristic viscosity and surface tension values depending on the chemical composition of cullet using a water glass solution are listed in Table 2. It is established that upon introduction of 10% sodium silicate to cullet, the deviation from the mean melting or softening temperature for characteristic viscosity values decreases by 15 – 19%; and the surface tension of glass melt decreases as well. The surface tension values in all glasses differ very little. It can be conjectured that the batch prepared from cullet of different chemical compositions after adding water glass becomes partly homogenized and the technological viscosity parameters become averaged, the temperature of foam glass swelling decreasing most perceptibly.

Modifications occurring in samples based on non-treated cullet powder and cullet powder treated with water glass heated to 1000°C are shown in Fig. 1. The thermograms of the two samples are similar. The DTA curve has endothermic effects at temperatures of 100, 600, and 960°C. However, the cullet treated with water glass gives an additional effect at temperatures of 160 and 760°C. Furthermore, the endothermic effect at 100°C in the cullet treated with water glass is

wider and the DTG curve shows that weight loss in the range of 100°C occurs at a variable rate. At least four acceleration and deceleration peaks of weight loss can be discriminated in the curve. The weight loss in both samples is registered up to approximately 700°C and under endothermic effects at 760 ad 960°C the weight of the samples does not change.

The endothermic effects, under which weight losses are registered, are related to removal of adsorbed water (the effect at 100°C) and for the cullet treated with water glass to dehydration of water glass and the products of water glass reacting with cullet particles. At 540 and 600–620°C chemically bonded water is released. The endothermic effect at 760°C is due to the melting of water glass and the products of reaction of glass with water glass, and the endothermic effect at 960°C is due to melting of glass that has not reacted.

The effect of water glass on the temperature of softening and swelling of cullet samples was investigated using a high-temperature microscope. It was established that formation of a porous structure in cullet treated with water glass proceeds in two stages. The first stage is characterized by an endothermic effect at 600°C (Fig. 1) and an increased sample volume within a temperature interval of 600–750°C (Fig. 2), as well as formation of a fine-pore cellular structure.

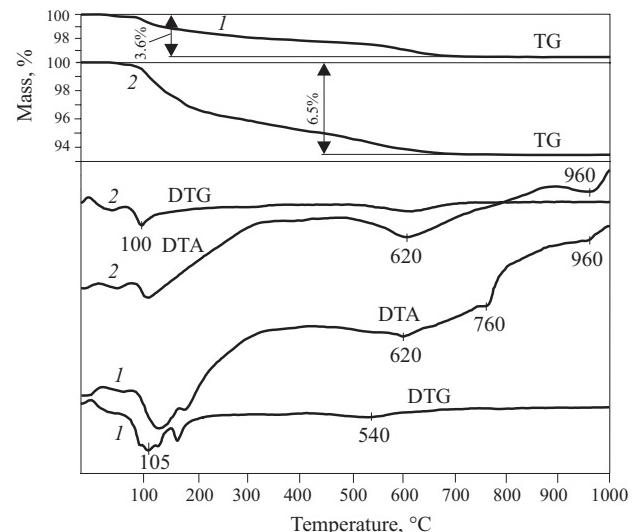


Fig. 1. Thermograms of non-treated cullet (1) and cullet treated with water glass (2).

The second stage is characterized by an endothermic effect at 760°C. The volume of the sample does not increase; however, a change in its relief contour at 795°C points to the for-

TABLE 2

Glass	Sodium silicate additive, %	Chemical composition, %	Temperature, °C, for typical viscosity, Pa · sec			Surface tension of melt, N/m
			10 ²	10 ⁴	10 ⁸	
Green bottle (Aleksotas glass works, Lithuania)	0	71.36 SiO ₂ , 6.31 CaO, 4.13 MgO, 0.39 Fe ₂ O ₃ , 3.80 Al ₂ O ₃ , 13.56 Na ₂ O, 0.11 Cr ₂ O ₃	1257	945	676	0.326
	10	71.53 SiO ₂ , 5.68 CaO, 3.72 MgO, 0.35 Fe ₂ O ₃ , 3.42 Al ₂ O ₃ , 14.89 Na ₂ O, 0.10 Cr ₂ O ₃	1237	927	659	0.323
Clear bottle (Aleksotas glass works, Lithuania)	0	73.00 SiO ₂ , 6.70 CaO, 3.79 MgO, 0.05 Fe ₂ O ₃ , 2.45 Al ₂ O ₃ , 14.37 Na ₂ O	1226	924	660	0.326
	10	73.01 SiO ₂ , 6.03 CaO, 3.41 MgO, 0.04 Fe ₂ O ₃ , 2.20 Al ₂ O ₃ , 15.62 Na ₂ O	1209	908	646	0.320
Clear container (Panevezhio stiklas, Lithuania)	0	72.72 SiO ₂ , 1.49 Al ₂ O ₃ , 10.45 CaO, 1.44 MgO, 13.80 Na ₂ O	1203	915	662	0.322
	10	72.76 SiO ₂ , 1.34 Al ₂ O ₃ , 9.45 CaO, 1.29 MgO, 15.11 Na ₂ O	1191	902	648	0.322
Window (Panevezhio stiklas, Lithuania)	0	72.70 SiO ₂ , 7.80 CaO, 3.65 MgO, 0.14 Fe ₂ O ₃ , 1.50 Al ₂ O ₃ , 13.70 Na ₂ O	1218	923	663	0.324
	10	72.74 SiO ₂ , 7.02 CaO, 0.13 Fe ₂ O ₃ , 3.28 MgO, 1.35 Al ₂ O ₃ , 15.02 Na ₂ O	1202	907	648	0.320
Mean value and deviations	0	SiO ₂ – 72.44 $\frac{+0.56}{-1.08}$, CaO – 7.81 $\frac{+2.64}{-150}$, MgO – 3.25 $\frac{+0.88}{-1.81}$, Al ₂ O ₃ – 2.31 $\frac{+1.49}{-0.82}$, Na ₂ O – 13.86 $\frac{+0.51}{-0.30}$	1226 $\frac{+31}{-23}$	927 $\frac{+18}{-12}$	665 $\frac{+11}{-5}$	0.324
	10	SiO ₂ – 72.51 $\frac{+0.50}{-0.98}$, CaO – 7.04 $\frac{+2.41}{-1.36}$, MgO – 2.92 $\frac{+0.80}{-1.63}$, Al ₂ O ₃ – 2.08 $\frac{+1.34}{-0.74}$, Na ₂ O – 15.16 $\frac{+0.46}{-0.27}$	1210 $\frac{+27}{-19}$	911 $\frac{+16}{-9}$	650 $\frac{+9}{-4}$	0.321

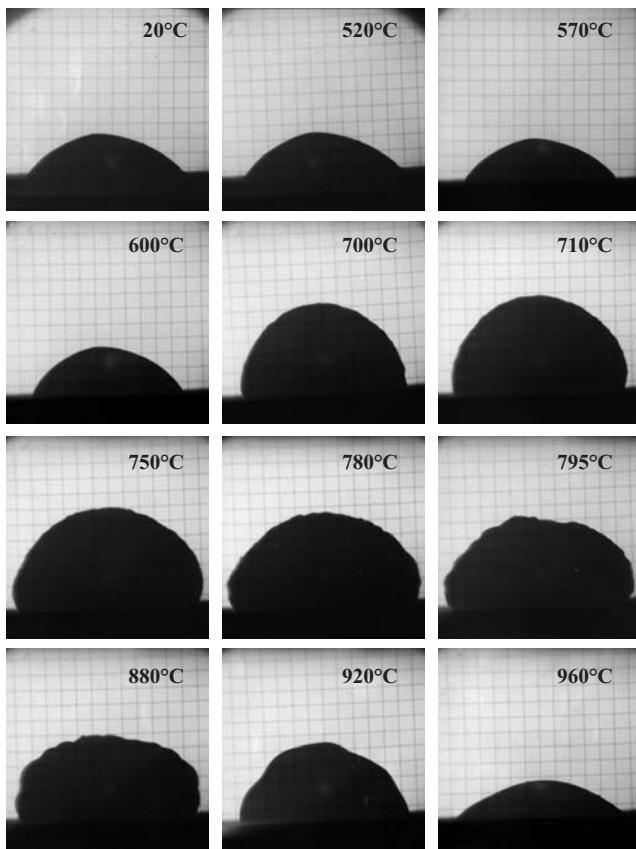


Fig. 2. Results of studying cullet treated with water glass using a high-temperature microscope.

mation of a coarse-pore cellular structure. The shrinkage of the sample at 880°C is determined by melting of water glass and the products of the reaction of glass with water glass.

The diffraction pattern of non-treated cullet (Fig. 3) exhibits the presence only of the crystalline phases (metallic iron and quartz) formed in the course of cullet milling. After heating to 1000°C wollastonite crystallizes from glass. Metallic iron does not get oxidized. The diffraction pattern of cullet treated with water glass in addition to quartz and metallic iron has weak and wide maxima of calcite CaCO_3 . After roasting to a temperature of 1000°C diopside $\text{CaMg}[\text{Si}_2\text{O}_6]$ crystallizes from glass. Metallic iron does not get oxidized either.

The nature of dehydration and the data of x-ray phase analysis indicate that water glass reacts with glass particles already at room temperature. Sodium ions push calcium ions from the glass structure and deeper dehydration of glass takes place. Sintering and melting of particles of water glass and products saturated with sodium ions during the reaction of glass with water glass take place at temperatures of 600 and 760°C. The liquid-phase material in the course of melting fills the space between the particles of treated cullet and thus hampers the release of the gaseous phase, as a consequence of which the material starts swelling (Fig. 2).

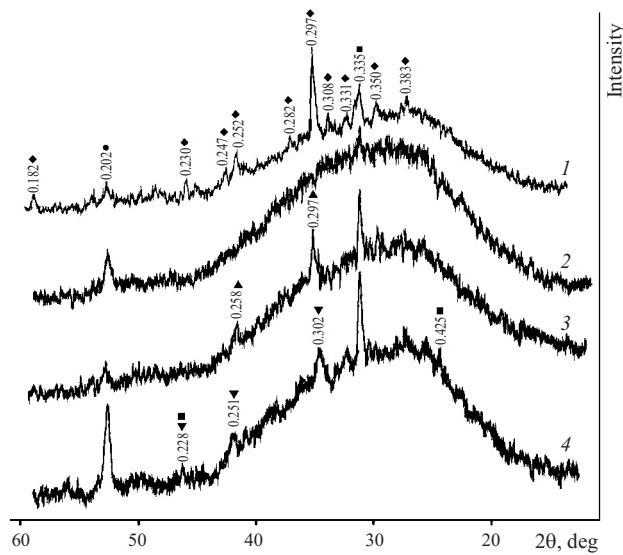


Fig. 3. Results of x-ray analysis of non-treated cullet fired at 1000°C (1), non-treated cullet (2), cullet treated with water glass after firing at 1000°C (3), and cullet treated with water glass (4): ♦) wollastonite; ●) metallic iron; ■) quartz; ▽) calcite; ▲) diopside.

Thus, introduction of sodium silicate in the form of an aqueous solution of water glass into a foam glass batch makes it possible to homogenize the chemical composition of cullet of different grades. A complex physicochemical process takes place, as a consequence of which milled cullet is partly destroyed and the chemical composition of the batch and its most essential technological properties are homogenized. The chemical interaction between water glass and the surface of milled cullet particles produces silicates containing bound water, which is released at high temperatures (600 – 620°C) and contributes to foam glass frothing. Water glass in a batch increases the amount of the vitreous phase and decreases the propensity of glass to crystallization.

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